



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CENTER FOR ENVIRONMENTAL MEASUREMENT AND MODELING
RESEARCH TRIANGLE PARK, NC 27711

OFFICE OF
RESEARCH AND DEVELOPMENT

January 30, 2020

Mr. Clark Freise, Assistant Commissioner
New Hampshire Department of Environmental Services (NHDES)
29 Hazen Drive
P.O. Box 95
Concord, New Hampshire 03301

Dear Mr. Freise:

I am pleased to provide the enclosed 7th report from our ongoing collaborative technical support to NHDES assisting with concerns over per- and polyfluorinated alkyl substances (PFAS) environmental contamination associated with manufacturing sites. This report is in response to your August 2017 request asking for laboratory assistance analyzing per- and polyfluoroalkyl substances (PFAS) in various environmental media near an industrial site. The enclosed Report #7 provides non-targeted analysis laboratory results that tentatively identify various PFAS found in surface and groundwater samples.

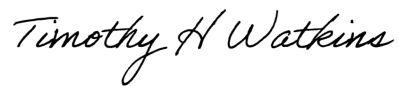
It is our understanding that this information was requested by NHDES to help in their ongoing investigation into the presence of PFAS in the environment near manufacturing facilities of interest. This request relates to our research capabilities and interests applying targeted and non-targeted analytical methods for discovery of the nature and extent of PFAS environmental occurrence that may be potentially associated with industrial releases. EPA continues to develop analytical methods for many PFAS compounds in various media including some of those included in this report. We are providing the results of our analysis as they become available.

In this report, we provide PFAS tentative identification and non-quantitative analytical results. We do not interpret exposure or risk from these values. EPA does not currently have health-based standards, final toxicity factors, or associated risk levels for PFAS, other than perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and perfluorobutanesulfonic acid (PFBS). While the data provided in the attached reports indicate the presence (or lack) of PFAS in the water samples, we do not have sufficient information to offer interpretations related to human or environmental exposure and risk.

Thank you for inviting us to be part of this effort that helps to further both EPA's and New Hampshire's understanding of an important issue in the state. This is one of a number of Agency efforts that continue EPA's commitment to cooperative federalism.

If you have any questions or concerns, do not hesitate to contact me at (919) 541-2107 or via email at Watkins.tim@epa.gov or Brian Schumacher at (702) 798-2242 or via email at Schumacher.brian@epa.gov. I look forward to our continued work together.

Sincerely,

A handwritten signature in black ink that reads "Timothy H. Watkins". The script is cursive and fluid, with the first letters of each word being capitalized and prominent.

Timothy H. Watkins
Director

CC:

Meghan Cassidy, USEPA, Region 1
Deb Szaro, USEPA, Region 1
Jennifer McLain, USEPA OW
Mike Koerber, USEPA OAR
Jeff Morris, USEPA OPPT
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PFAS Environmental Contamination Associated with Manufacturing Sites in New Hampshire

Laboratory Data Report #7: Non-targeted Analysis of PFAS in Water Samples

Background. The New Hampshire Department of Environmental Services (NHDES), in coordination with EPA Region 1, requested the Office of Research and Development's (ORD's) technical support in analyzing per- and polyfluoroalkyl substances (PFAS) in manufacturing facilities and surrounding environmental media. NHDES assumed responsibility for the collection of samples and their shipment to the ORD laboratory. ORD was responsible for sample extraction and analysis. ORD's analysis and report team that contributed to this effort are listed in Table 1.

Table 1. EPA Office of Research and Development Lab Analysis and Report Team.

Responsibility	Personnel
ORD Principal Investigators	Andy Lindstrom, Mark Strynar, and John Washington
Laboratory chemistry	Mark Strynar, James McCord
Quality Assurance Review	Christine Alvarez, Sania Tong Argao
Management coordination and review	Myriam Medina-Vera, Tim Buckley, Kate Sullivan
Report preparation	Kate Sullivan

This 7th report includes non-targeted analysis (NTA) results for 25 water samples and a trip blank collected from surface and ground water near an industrial site in New Hampshire. Samples were collected September 27, 2017 by NHDES. EPA/ORD Report #3¹ provided concentrations for 11 PFAS for the same samples using targeted analysis based on standards for the quantitation of the PFAS present in the samples. In contrast, this report presents NTA for the samples in which the presence or absence of a PFAS is identified and relative abundances (i.e., semiquantitative) of the PFAS are presented.

The current data report provides a simple representation and summary of NTA results. Therefore, the description of methods and quality assurance are brief and high-level. Additional reports and/or publications may be developed that will include a more detailed description of methods, quality assurance procedures, and statistical interpretation of the data. As study partners/collaborators, we anticipate that NHDES and Region 1 will assist in these reports and publications.

Methods in Brief. Water samples were analyzed with ultra-performance liquid chromatography mass spectrometry (UPLC-MS) using methods described within our project Quality Assurance

¹ EPA/ORD NH Report #3. Technical support to New Hampshire—Targeted PFAS Measurements in Water. October 4, 2018.

Project Plan (QAPP)², our laboratory QAPP³, and McCord *et al.* 2019.⁴ In brief, water samples (500 mL) were filtered and then extracted using a WAX solid phase extraction cartridge. PFAS was removed from the cartridge in methanol and reduced to a volume of 1 mL under a gentle stream of nitrogen. An aliquot of the 1 mL concentrated sample was injected into an Agilent 1100 high performance liquid chromatograph (HPLC) coupled to an Agilent 6210 Time-of-Flight mass spectrometer (TOFMS). PFAS were analyzed using our non-targeted analysis (NTA) workflow.

NTA provides two important measurements. The first is a tentative identification of PFAS detected in the sample. PFAS are tentatively identified based on a combination of highly-resolved mass (Daltons to 4 decimal places) of the chemical along with patterns of fragmentation compared to on-line and in-house mass-spectral libraries. PFAS chemical identification is determined to various levels of confidence depending on the strength of evidence from automated and manual examination fragmentation spectra and/or comparison with mass spectral libraries.

The second measurement is an indication of the relative abundances of the PFAS present in the sample. The mass spectrometer detector provides integrated peak areas for the chromatogram of the compound mass (± 5 ppm) at the specified retention time. The peak area counts are proportional to the mass of PFAS in the sample. Since the sample and injection volumes are held constant, the peak area counts are also proportional to concentration, although the relationship varies based on compound.

It is important to understand how results of NTA differ from those produced with routine laboratory target analysis. Without a standard curve to calibrate the relationship between peak area and a true mass or concentration value, the peak area counts alone should be considered a semi-quantitative indicator of relative abundance. Analyte peak areas can be compared between samples in a sample set to obtain relative concentrations but cannot be directly compared between analytes. Our experience indicates that measured abundances for PFAS are four to six orders of magnitude higher than the ppt concentration (e.g. $1 \times 10^7 \sim 100$ ppt) not accounting for any dilutions during sample preparation. Peak area counts are expected to have much greater sampling and analytical variability. For example, it is possible for field duplicates to differ by

² National Exposure Research Laboratory, Quality Assurance Project Plan: Non-Targeted Analyses of Per- and Polyfluoroalkyl Substances (PFAS) for New Hampshire Department of Environmental Services (NHDES), D-EMMD-PHCB-015-QAPP-01, October 2, 2017.

³ National Exposure Research Laboratory, Quality Assurance Project Plan: Non-Targeted Analyses of Per and Polyfluoroalkyl substances (PFAS) in Liquid Samples J-WECD-0031919-QP-1-0, September 18, 2019.

⁴ McCord, J., Strynar, M. Identifying Per- and Polyfluorinated Chemical Species with a Combined Targeted and Non-Targeted-Screening High-Resolution Mass Spectrometry Workflow. *J. Vis. Exp.* (146), e59142, doi:10.3791/59142 (2019). <https://www.jove.com/video/59142/identifying-per-polyfluorinated-chemical-species-with-combined>

two or three-fold or more. Any application of NTA results should consider this inherently greater uncertainty.

The NTA data generated by LC/MS were considered as a “detect” when acceptable chromatographic peaks and spectra were evident. Samples without a detectable peak are reported as “ND”. Samples with detected analytes were further screened to determine the reporting limit (RL) that accounts for contamination that may have occurred during sampling and analysis including field, laboratory, and instrument blanks. The RL was established for each compound by statistical analysis of the combined laboratory and field blanks, where $RL = AVE [\text{blanks}] + 3 \times STD [\text{blanks}]$. Sample values less than this statistically defined threshold are reported as “<RL”.

Summary of Results

Compound Identification. Across all the water samples, the 24 PFAS listed in Table 2 we detected and tentatively identified by chemical formula, name, CAS registry number (CASRN), monoisotopic mass and retention time. Within the table, we have ordered PFAS by homologous series:

- 1) carboxylic acids (#1-10);
- 2) sulfonic acids (#11-14); and
- 3) the remainder ordered by monoisotopic mass (#15-24).

A larger number of chemical features likely to be PFAS (or breakdown products) were present, but we report these 24 based on criteria of abundance (or peak area) and high confidence in tentative identification. PFAS with CASRN are registered in EPA’s Chemistry dashboard (<https://comptox.epa.gov/dashboard>) where additional information about these chemicals can be found (U.S. EPA CompTox, 2019)⁵.

Abundance of Compounds. In Table 3, we provide results for the 24 PFAS identified in Table 2 for 25 water samples and a trip blank (TB). Results are given as peak area counts superimposed on a heat map where gradations in color reflect seven classifications of peak area from low (non-detect) to high (>1,000,000). The heat map is useful in showing where PFAS “light-up” in terms of detection and high peak areas. Heatmap values >50,000 (yellow, orange and red tones) have the highest confidence that a compound is present in relatively greater abundance.

None of the PFAS compounds were detected at levels greater than the reporting limit in the field blanks. There are few QA/QC performance criteria available for NTA. The relative percent difference (RPD) of the field duplicate pairs is a measure of reproducibility in the samples. The RPD of analytes greater than RL averaged 25% for the sample pair EPAORD004/EPAORD005,

⁵ U.S. EPA CompTox Chemicals Dashboard <https://comptox.epa.gov/dashboard>

and 43% for the sample pair EPAORD012/EPAORD013. Both met the project goal of RPD <50%.

The highest peak areas were generally observed for the carboxylic acids and sulfonic acid compounds (Chem. Ref. #1-14) for which concentrations determined with authentic standards were previously reported in ORD NH Report #3⁶. Other PFAS (Chem. Ref. #15-24) were found at various abundances within the samples. For compounds evaluated in both targeted analysis and NTA, results are qualitatively similar in that the same compounds were generally more abundant in the same samples. However, NTA often did not detect compounds quantitated at low concentrations with targeted analysis.

⁶ ORD NH Report #3: Technical Support to New Hampshire DEP-Targeted PFAS Measurements in Waters. October 4, 2018.

Table 2. PFAS Tentatively Identified in Water Samples by Non-Targeted Analysis.

Chem Ref. #	Tentatively Identified Compound Name	CAS Number	Formula	Monoisotopic Mass (Daltons)	Retention Time
1	Perfluorobutanoic acid (PFBA)	375-22-4	C ₄ H F ₇ O ₂	213.9866	1.52
2	Perfluoropentanoic acid (PFPeA)	2706-90-3	C ₅ H F ₉ O ₂	263.9830	3.68
3	Perfluorohexanoate (PFHxA)	92612-52-7	C ₆ H F ₁₁ O ₂	313.9798	5.07
4	Perfluoroheptanoic acid (PFHpA)	375-85-9	C ₇ H F ₁₃ O ₂	363.9765	5.82
5	(PFHpA-CO ₂ fragment)		C ₆ H F ₁₃	319.9867	5.81
6	Perfluorooctanoic acid (PFOA)	335-67-1	C ₈ H F ₁₅ O ₂	413.9733	6.33
7	(PFOA-CO ₂ fragment)		C ₇ H F ₁₅	369.9834	6.33
8	Perfluorononanoic acid (PFNA)	375-95-1	C ₉ H F ₁₇ O ₂	463.9697	6.76
9	(PFNA-CO ₂ fragment)		C ₈ H F ₁₇	419.9799	6.76
10	Perfluorodecanoic acid (PFDA)	335-76-2	C ₁₀ H F ₁₉ O ₂	513.9658	7.17
11	Perfluorobutanesulfonate (PFBS)	375-73-5	C ₄ H F ₉ O ₃ S	299.9497	4.22
12	Perfluoropentanesulfonate (PFPeS)	2706-91-4	C ₅ H F ₁₁ O ₃ S	349.9470	5.25
13	Perfluorohexane Sulfonate (PFHxS)	355-46-4	C ₆ H F ₁₃ O ₃ S	399.9434	5.88
14	Perfluorooctanesulfonate (PFOS)	1763-23-1	C ₈ H F ₁₇ O ₃ S	499.9362	6.75
15	3:2 Fluorotelomer alcohol	755-40-8	C ₅ H ₅ F ₇ O	214.0224	1.24
16	Perfluoro-3-(1H-perfluoroethoxy)propane	3330-15-2	C ₅ H F ₁₁ O	285.9851	5.33
17	Tridecafluoroheptaneperoxoic acid	139702-34-4	C ₇ H F ₁₃ O ₃	379.9712	5.98
18	Undecafluorocyclohexanemethanol dihydrogen phosphate	32582-74-4	C ₇ H ₄ F ₁₁ O ₄ P	391.9713	6.04
19	Perfluorohexanesulfonamide	41997-13-1	C ₆ H ₂ F ₁₃ N O ₂ S	398.9571	5.07
20	6:2 Fluorotelomer sulfonic acid (6:2FtS)	27619-97-2	C ₈ H ₅ F ₁₃ O ₃ S	427.9745	6.30
21	Perfluoropentane sulfonamido amine	68555-78-2	C ₁₀ H ₁₃ F ₁₁ N ₂ O ₂ S	434.0563	4.12
22	Perfluorooctanesulfonamide (PFOSA)	754-91-6	C ₈ H ₂ F ₁₇ N O ₂ S	498.9501	6.33
23	2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9-Hexadecafluorononyl methacrylate	1841-46-9	C ₁₃ H ₈ F ₁₆ O ₂	500.0217	6.75
24	POLYFLGSID_880958	72494-14-5	C ₃₃ H ₄₂ F ₈ N ₂ O ₄	682.3026	12.88

Table 3. Non-Targeted Analysis Semi-Quantitation (Peak Area Counts) of PFAS in Water Samples.

Chem Ref. #	EPAORD 001	EPAORD 002	EPAORD 003	EPAORD 004	EPAORD 005	EPAORD 006	EPAORD 007	EPAORD 008	EPAORD 009	EPAORD 010	EPAORD 011	EPAORD 012	EPAORD 013
1	40,400	13,900	12,900	149,000	183,000	686,000	21,200	20,300	154,000	104,000	248,000	45,600	53,200
2	102,000	15,700	16,600	670,000	838,000	2,970,000	62,100	38,000	371,000	356,000	997,000	126,000	153,000
3	173,000	19,500	15,000	826,000	1,010,000	4,260,000	103,000	57,600	562,000	632,000	1,870,000	218,000	266,000
4	229,000	<RL	<RL	616,000	765,000	2,760,000	155,000	81,600	464,000	689,000	1,800,000	421,000	490,000
5	103,000	8,710	6,030	258,000	312,000	984,000	70,900	41,200	162,000	284,000	624,000	211,000	178,000
6	1,010,000	38,200	19,700	2,610,000	3,250,000	11,800,000	495,000	266,000	2,290,000	2,440,000	6,600,000	1,580,000	2,260,000
7	504,000	20,600	10,300	1,210,000	1,470,000	4,810,000	272,000	172,000	1,060,000	1,210,000	3,040,000	1,010,000	1,160,000
8	182,000	40,500	16,200	43,800	45,300	95,700	5,700	ND	15,500	11,000	6,300	ND	ND
9	85,700	19,500	7,740	23,600	26,600	55,600	ND	ND	13,000	6,030	ND	ND	ND
10	183,000	41,800	152,000	149,000	53,700	41,100	ND	ND	ND	6,380	ND	ND	ND
11	42,500	10,400	10,600	61,200	112,000	64,000	36,500	22,300	70,800	79,100	152,000	43,900	53,600
12	21,700	ND	ND	33,300	38,900	62,000	10,500	6,860	5,850	20,000	76,000	52,700	67,100
13	120,000	12,000	8,650	101,000	128,000	184,000	38,600	19,500	36,200	51,000	118,000	649,000	870,000
14	327,000	62,500	147,000	444,000	451,000	2,530,000	19,300	61,200	21,100	11,600	25,000	74,100	95,300
15	135,000	199,000	180,000	108,000	146,000	16,800	ND	ND	4,140	8,900	5,850	2,050	ND
16	8,260	6,920	ND	5,610	ND	8,000	5,750	ND	ND	5,600	7,030	4,130	6,680
17	35,200	12,100	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
18	9,270	ND	ND	18,100	22,000	64,800	8,110	ND	9,060	25,900	78,300	ND	ND
19	5,650	ND	ND	21,900	22,200	81,100	ND	ND	13,100	22,000	67,800	8,170	9,020
20	ND	ND	ND	26,100	33,400	646,000	ND	ND	ND	ND	ND	ND	ND
21	16,600	ND	ND	20,200	29,100	15,100	41,100	16,000	19,900	ND	ND	3,330	ND
22	53,700	ND	ND	117,000	118,000	233,000	33,200	21,300	89,600	128,000	306,000	113,000	121,000
23	15,900	4,380	1,780	8,910	14,300	156,000	ND	1,150	ND	ND	ND	3,150	8,740
24	172,000	154,000	153,000	556,000	649,000	622,000	584,000	538,000	626,000	528,000	303,000	258,000	454,000

LEGEND	
Color	Peak Area Category
ND	No peak area detected
<RL	Less than the Reporting Limit
	>RL - 50,000
	50,000 - 100,000
	100,000 - 200,000
	200,000 - 500,000
	500,000 - 1,000,000
	>1,000,000

Table 3. (continued). Non-Targeted Analysis Peak Area Counts of PFAS in Water Samples.

Chem Ref. #	EPAORD 014	EPAORD 015	EPAORD 016	EPAORD 017	EPAORD 018	EPAORD 019	EPAORD 020	EPAORD 021	EPAORD 022	EPAORD 023	EPAORD 024	EPAORD 901	TB
1	8,710	29,700	29,500	35,500	15,000	37,100	23,000	23,400	60,400	89,400	30,900	21,100	ND
2	6,270	88,200	81,300	59,000	18,000	84,800	38,600	38,000	179,000	357,000	66,800	55,600	ND
3	5,610	96,200	151,000	110,000	26,900	108,000	48,400	51,900	219,000	481,000	76,700	155,000	ND
4	<RL	101,000	175,000	197,000	57,500	136,000	71,600	78,200	281,000	669,000	91,300	345,000	ND
5	4,120	44,400	81,000	67,300	24,400	55,300	33,600	30,200	125,000	248,000	45,700	141,000	ND
6	41,600	445,000	542,000	1,090,000	378,000	528,000	356,000	351,000	842,000	3,120,000	211,000	2,370,000	ND
7	23,200	237,000	300,000	525,000	206,000	265,000	185,000	186,000	439,000	1,450,000	126,000	1,060,000	ND
8	ND	ND	3,500	5,140	ND	6,540	6,240	5,850	7,310	8,530	ND	6,680	ND
9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
11	8,770	65,200	82,800	258,000	38,700	428,000	24,900	11,500	118,000	14,100	14,500	13,400	ND
12	ND	ND	9,260	9,340	7,810	7,570	7,430	ND	11,900	6,900	7,030	ND	ND
13	5,610	22,100	19,500	38,700	30,100	27,900	29,600	24,000	42,800	42,100	30,400	29,200	ND
14	ND	17,800	ND	34,300	14,900	11,700	17,300	13,800	5,670	25,600	7,890	44,700	ND
15	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1,850	ND	ND
16	6,600	6,430	48,500	7,080	7,250	7,020	9,480	6,950	10,300	11,000	7,520	8,140	ND
17	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
18	ND	ND	ND	ND	ND	ND	ND	ND	ND	17,900	ND	9,230	ND
19	ND	ND	6,700	ND	ND	ND	ND	ND	6,130	10,800	ND	ND	ND
20	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
21	ND	7,580	6,840	36,400	155,000	9,610	11,400	15,500	11,700	ND	17,000	25,800	ND
22	ND	30,700	30,200	58,100	23,000	31,500	21,800	21,200	39,900	116,000	13,900	99,400	ND
23	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4,310	ND
24	410,000	332,000	360,000	306,000	525,000	224,000	318,000	283,000	331,000	257,000	219,000	225,000	<RL

LEGEND	
Color	Peak Area Category
ND	No peak area detected
<RL	Less than the Reporting Limit (RL)
	>RL - 50,000
	50,000 - 100,000
	100,000 - 200,000
	200,000 - 500,000
	500,000 - 1,000,000
	>1,000,000